PB-242 970

CARBON, NITROGEN, AND PHOSPHORUS REMOVAL IN STAGED NITRIFICATION-DENTRIFICATION TREATMENT

James A. Heidman, et al

District of Columbia Department of
Environmental Services

Prepared for:

National Environmental Research Center

June 1975

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192172

PB 242 970

EPA-670/2-75-052
June 1975

Environmental Protection Technology Series

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EPA-670/2-75-052
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By

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FOREWORD

Man and his environment must be protected from the adverse effects of pesticides, radiation, noise and other forms of pollution, and the unwise management of solid waste. Efforts to protect the environment require a focus that recognizes the interplay between the components of our physical environment--air, water, and land. The National Environmental Research Centers provide this multidisplinary focus through programs engaged in

- studies on the effects of environmental contaminants on man and the biosphere, and
- a search for ways to prevent contamination and to recycle valuable resources.

This work describes an advanced biological treatment system to remove organic, nitrogen and phosphorus pollutants from the aqueous environment. The complex approach provides the maximum possible biological treatment reliability for treatment of municipal wastewaters and may be used in future wastewater reuse systems for recycle of our water resources.

A. W. Breidenbach, Ph.D.
Director
National Environmental
Research Center, Cincinnati

ABSTRACT

A three-stage activated sludge system with mineral addition for nutrient removal was operated with District of Columbia primary effluent. Influent flow followed a programmed diurnal cycle and averaged 205 m^3/day (54,000 gpd). The first biological reactor was operated as a modified aeration system with ferric chloride addition for supplemental phosphorus removal. The clarified effluent then flowed to the second reactor for the biological nitrification of ammonia and organic nitrogen. Dry lime was used for pH control. Methanol was added to the nitrified effluent, and biological denitrification occurred in the final activated sludge system. Prior to clarification, the denitrification effluent was briefly aerated for nitrogen gas removal and for consumption of any excess methanol. The clarified effluent was then split into two equal streams for comparison of filtration performance of a dual-media coal and sand filter with that of a multi-media coal, sand, and ilmenite filter. Effluent quality consistently met the proposed D.C. discharge standards of BOD $\leq$ 4.5 mg/l; total N $\leq$ 2.5 mg/l; and P $\leq$ 0.22 mg/l.

This report was submitted in partial fulfillment of Contract No. 68-01-0162 by the Department of Environmental Services, Government of the District of Columbia, under the sponsorship of the Environmental Protection Agency. Work was completed as of September 1973.

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ACKNOWLEDGMENT

The assistance of the District of Columbia operators, technicians and laboratory staff at the EPA-DC Pilot Plant is gratefully acknowledged.

SECTION I

CONCLUSIONS

The three-stage activated sludge system with final filtration is entirely satisfactory for meeting the proposed District of Columbia discharge standards. This system was the one selected for the 812 m^3/min (309 mgd) Blue Plains Sewage Treatment Plant.

Specifically, the modified aeration operated at an SRT of approximately 1 day with mineral addition exhibited excellent stability and produced a satisfactory effluent for the subsequent processes in the three stage system. With $FeCl_3$ dosage equal to a 1:1 mole ratio Fe/P, modified aeration removed approximately 81% of the BOD_5, 72% of the phosphorus, and about 31% of the total nitrogen.

The subsequent nitrification process with the pH controlled to 7.0-7.2 by an average addition of 60 mg/l of dry CaO produced essentially complete nitrification (average residual TKN of 1.2 mg/l, excluding an upset from mechanical failure) and produced essentially complete removal of carbonaceous BOD_5 (nitrifier inhibited BOD_5 residual of approximately 3 mg/l). Batch nitrification kinetics on the process mixed liquor provided a strong correlation (correlation coefficient r = 0.837) between the nitrification rate constant and temperature. The relationship is:

$$K_{NH_3\text{-}N} = 0.0171\ t - 0.114$$

where $K_{NH_3\text{-}N}$ = gm NH_3-N/day/gm MLVSS

t = Temperature, ^oC

The denitrification process with methanol addition and with alum addition removed an average of 94% of the nitrate nitrogen with an annual average of 0.72 mg/l of residual NO_3-N. A dosage of four units of methanol (by weight) per unit of NO_3-N produced essentially complete denitrification. Batch denitrification kinetics tests on the process mixed liquor produced a moderately weak correlation (r = 0.629) between the denitrification rate constant and temperature. The relationship is:

$$K_{NO_3^-N} = 0.0212\ t - 0.1657$$

where $K_{NO_3^-N}$ = gm NO_3-N/day/gm MLVSS

t = temperature, ^oC

The alum addition in the denitrification process at an Al:P mole dosage ratio between 3:1 and 5:1 reduced the influent phosphorus by about 40% from about 3.4 mg/l to 2.1 mg/l as $PO_4^{\equiv}$. The real impact of the alum addition in denitrification was to insure good phosphorus and solids

removal by the final filtration process.

Dual- or multi-media filtration of the denitrified effluent produced a final effluent that consistently exceeded the discharge standards for the proposed new plant in Washington, D.C. The residual BOD_5 averaged 2 mg/l; the total nitrogen, 1.6 mg/l; and the total phosphorus, 0.52 mg/l as $PO_4^{\equiv}$.

SECTION II

RECOMMENDATIONS

Considering the length of time over which the three-stage activated sludge process was evaluated, there is little doubt that it will produce a high quality effluent throughout the year on District of Columbia wastewater. Therefore, further work is not needed to establish the basic reliability of the process.

There are, however, several areas that need to be explored so that the process operation can be optimized. The minimum methanol dosage needs to be ascertained more carefully. The possibility of varying the ferric chloride and alum feed in direct response to the incoming phosphate also requires study. Finally, it may not be necessary to add lime to the nitrification process, especially in the summer, and this could result in additional cost savings. Once the main District of Columbia treatment plant is constructed, all of these areas could be fully evaluated under full-scale operating conditions.

SECTION III

INTRODUCTION

The three-stage activated sludge system was examined on a pilot-plant scale as one of several process alternatives that could potentially meet the proposed discharge standards for the District of Columbia Blue Plains Wastewater Treatment Plant. These standards, which apply year-around, call for a maximum effluent BOD of 4.5 mg/l; total nitrogen not to exceed 2.5 mg/l; and total phosphate of less than 0.67 mg/l (0.22 mg/l of P). The three-stage system was put on stream in 1970 and was operated through September of 1973. This report summarizes the results obtained from the last year of operation, i.e., October 1972 through September 1973.

The three-stage biological system[1] consisted of modified aeration with mineral ($FeCl_3$) addition for removal of organic carbon and phosphorus; nitrification with lime addition for oxidation of ammonia to nitrate under controlled pH; denitrification with methanol as an external carbon source for removal of nitrate and with alum addition for residual phosphorus removal; and finally, filtration for removal of residual solids (C, P and N).

SECTION IV

EXPERIMENTAL PLAN

A schematic diagram of the three-stage activated sludge process is presented in Figure 1. The influent process flow, consisting of a small portion of the primary effluent from the District of Columbia Blue Plains Wastewater Treatment Plant operating at 762 m^3/min (290 mgd), was pumped to the modified aeration reactor on the diurnal flow pattern shown in Figure 2. Average process flow was approximately 205 m^3/day (54,000 gpd). The modified aeration reactor consisted of three completely mixed passes of equal size in series with an effective total volume of 22.0 m^3 (5,820 gal). The reactor provided a detention time of 2.6 hours at average flow. Compressed air was supplied through perforated PVC pipe diffusers and the dissolved oxygen levels in each stage were maintained between 0.5 and 4.0 mg/l. Ferric chloride was added to the third pass of the reactor. The chemical dosage rate was manually changed three times per day to correspond to the diurnal flow pattern.

The modified aeration reactor effluent discharged to a circular peripheral feed clarifier with an effective surface area of 8.9 m^2 (96 ft^2). The area provided an average overflow rate of 21.2 m/day (520 gpd/ft^2). Recycle solids were returned at a reasonably constant percentage of influent flow with manual adjustment of the recycle pumping rate at the times indicated in Figure 2. A typical relationship between process flow and recycle flow is shown in Figure 3. Except for brief periods, the three time per day manual adjustment of the recycle flow provided a reasonably constant rate between influent and recycle flow. The various chemical feed rates (ferric chloride, methanol, and alum) were also manually changed three times per day. The relative relationship between process flow and chemical feed rate is also presented in Figure 3.

The effluent from the modified aeration clarifier was pumped to the second biological system for nitrification. The nitrification reactor consisted of four complete mix passes operated in series. Total effective volume was 29.3 m^3 (7,740 gal), which provided for an average detention time of 3.4 hours. Air was supplied independently to each pass through perforated PVC pipe diffusers and the D.O. was maintained between 0.5 and 4.0 mg/l. A dry lime feeder was located above the first pass and lime was automatically fed to maintain the desired effluent pH.

The nitrified effluent flowed to a circular center-feed clarifier with a surface area of 8.9 m^2 (96 ft^2). Recycle solids were returned from the clarifier to the reactor at a constant rate that was not varied in response to the diurnal flow pattern. However, the recycle rate was changed from time to time as operating conditions warranted.

Methanol was added to the effluent from the nitrification clarifier and process flow was sent to the denitrification reactor. The denitrification reactor consisted of four, covered, mechanically stirred tanks of equal size in series. The tanks were covered to exclude oxygen transfer from

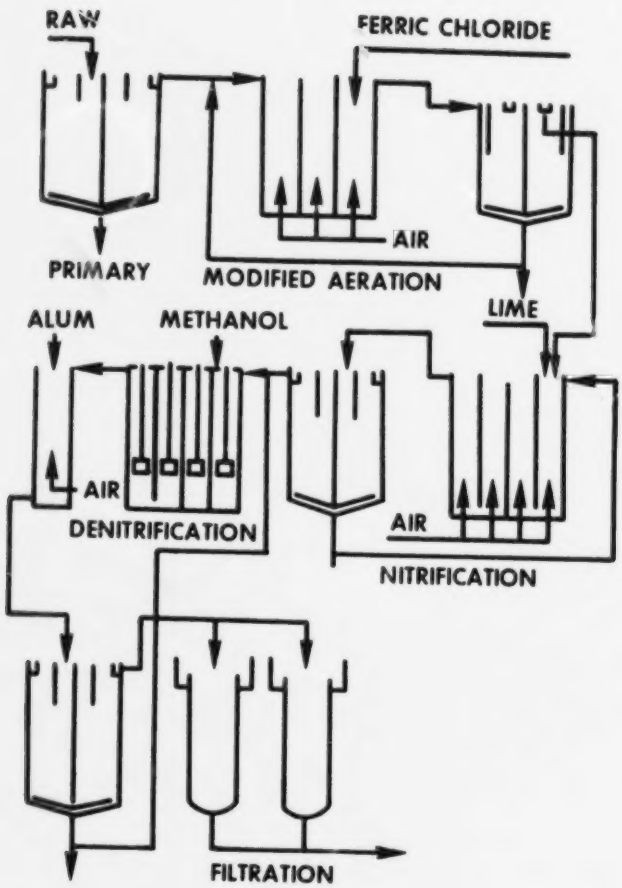

Figure 1. Flow diagram for three-stage activated sludge treatment

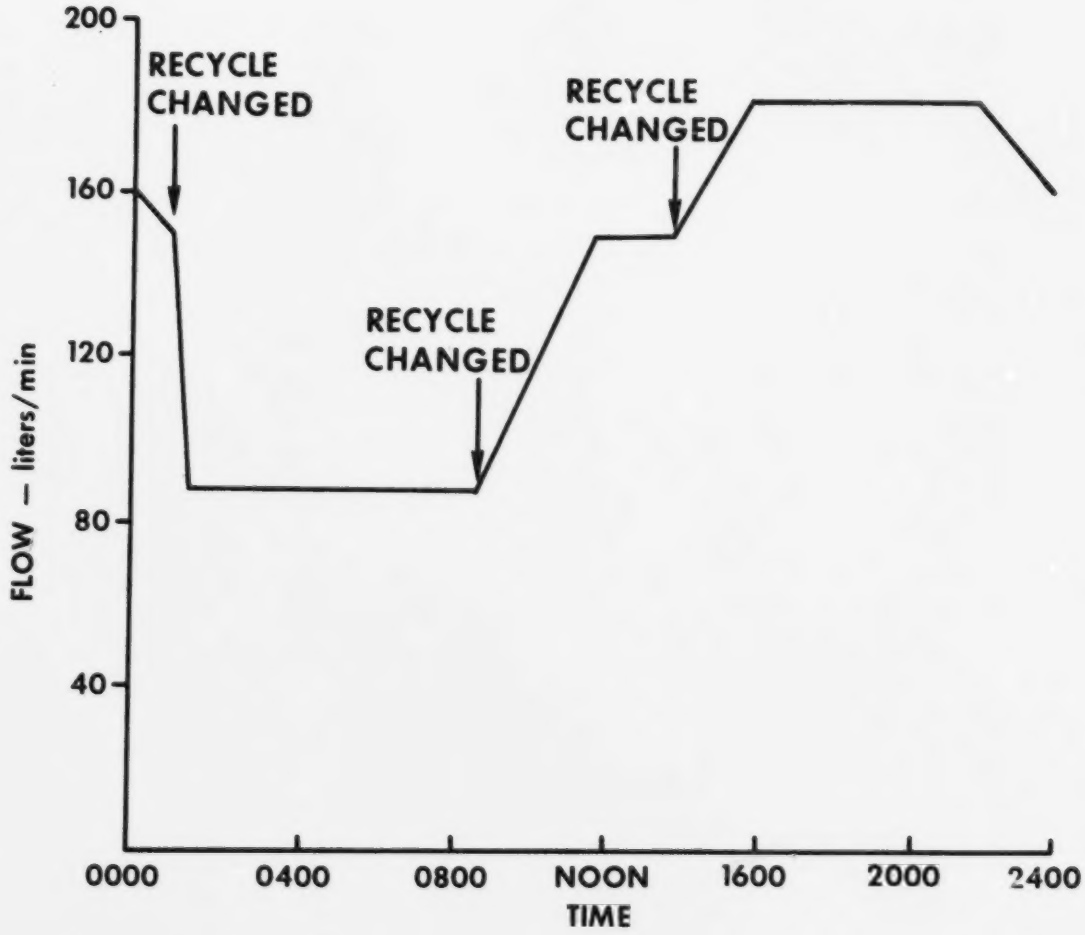

Figure 2. Diurnal flow pattern

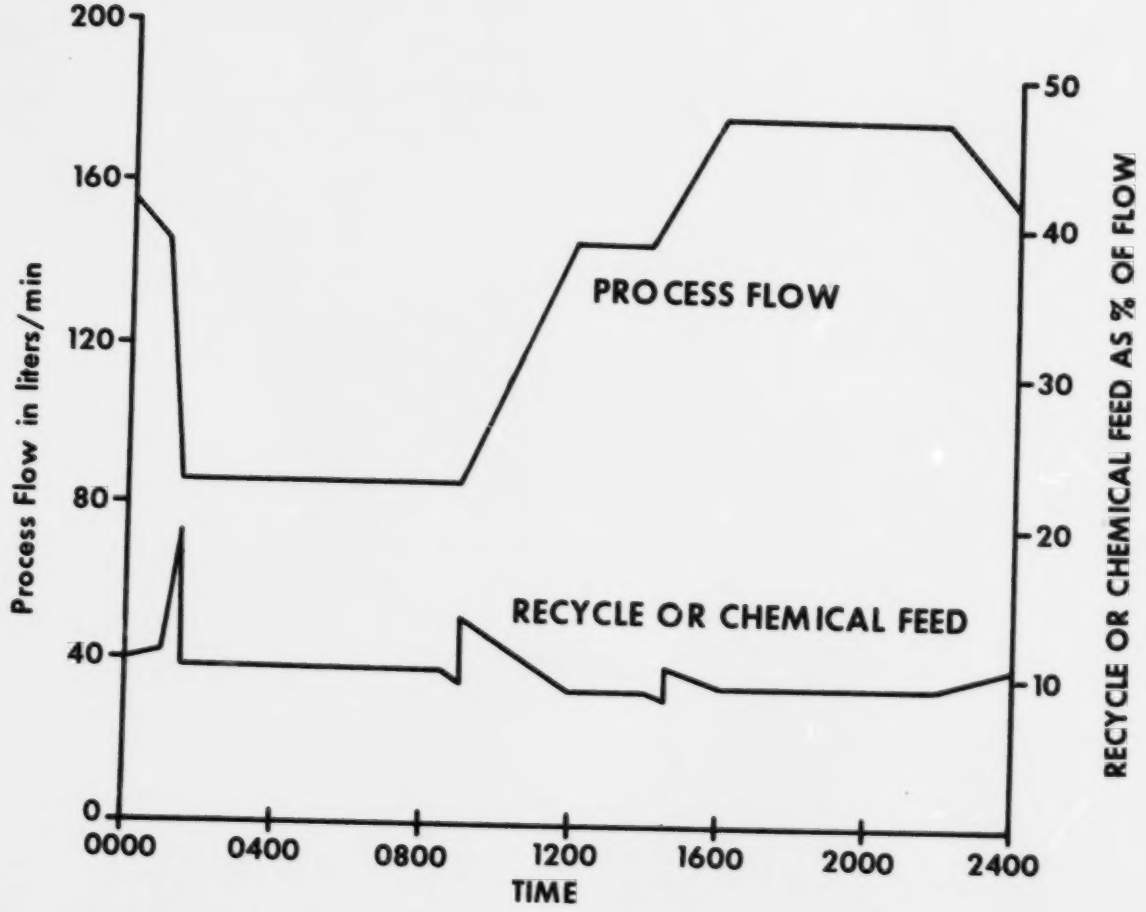

Figure 3. Diurnal flow pattern and relative recycle on chemical feedrate

the air. The total effective volume of the reactor was 27.3 m^3 (7,210 gal), with a corresponding detention time of approximately 3.2 hours.

Denitrified effluent flowed directly into a single, aerated, completely mixed chamber with an effective volume of 4.35 m^3 (1,150 gal). The purpose of the chamber was to strip nitrogen gas from the water and to oxidize any excess methanol that was not consumed in the denitrification reactor. Alum was also added to the chamber at the particular dosage rate desired.

Following aeration, the denitrified effluent flowed to a circular center-feed clarifier with a 5.85 m^2 (63 ft^2) surface area. The corresponding average overflow rate was 32.2 m/day (790 gpd/ft^2). Recycle solids were returned from the clarifier to the denitrification reactor at a constant rate of flow.

Effluent from the denitrification clarifier flowed to a splitter box, where it was equally divided before flowing to a dual-media and multi-media filter. The dual-media filter consisted of 0.30 m (12 inches) of sand with an effective size of 0.6-0.7 mm overlain by 0.61 m (24 inches) of coal with an effective size of 1.2-1.4 mm. The multi-media filter consisted of 0.08 m (3 inches) of ilmenite with an effective size of 0.2-0.35 mm; overlain by 0.23 m (9 inches) of sand of effective size 0.4-0.5 mm; overlain by 0.20 m (8 inches) of coal of effective size 1.0-1.1 mm; overlain by 0.41 m (16 inches) of coal with an effective size of 1.5-1.6 mm. The uniformity coefficient of all materials in the multi-media filter was 1.8. Filter loading varied from a low of 111 m/hr (1.9 gpm/ft^2) at low flow to a high of 235 m/hr (4.0 gpm/ft^2) at high flow. The average loading was 176 m/hr (3 gpm/ft^2). Differential pressure readings were taken at various bed depths, and the filters were backwashed either when the total pressure drop reached 3.0 m (120 inches) or after 24 hours even though the 3.0 m (120 inch) pressure drop had not yet been attained.

SECTION V

METHODS AND PROCEDURES

The process was operated on a 24-hour a day, 7-day a week schedule for the entire year of operation covered in this report. The only interruptions in the normal operating sequence resulted from mechanical malfunctions and these were of short duration.

Grab samples of influent, effluent, mixed liquor, etc., were taken every 4 hours. The samples collected for laboratory analysis were composited over a 24-hour period on Tuesday, Wednesday, and Thursday; samples collected on Friday-Saturday and on Sunday-Monday were composited over the 48-hour period. The single exception to this was that the samples for BOD analysis were just 24-hour composites and the analysis was always started within a few hours (4-10 hours) after the last sample had been collected for the 24-hour composite. All samples were refrigerated at 2°C. In addition, all samples except those taken for BOD or suspended solids analysis were preserved with one drop of H_2SO_4 per 30 ml of sample while they were being held in storage. All laboratory analyses (except BOD) were performed on a Monday through Friday schedule.

The following analyses were performed in the EPA-DC Pilot Plant laboratories according to the procedures specified in Standard Methods[2]: suspended solids, volatile suspended solids, BOD, COD, and TKN. BOD analyses in which NO_3 production was inhibited by the addition of 0.5 mg/l of 1-allyl-2-thiourea were also performed. The procedures specified in the EPA Manual[3] were used for the following: TOC with a Beckman analyzer; total solids; and NH_3, NO_3, NO_2 with a Technicon autoanalyzer. The method of Gales et al.,[4] was used for the determination of total phosphorus.

In addition to collecting samples for laboratory analysis every four hours, the operating personnel checked the dissolved oxygen levels in the appropriate reactors with a portable field probe and adjusted the air flow rates as necessary; obtained solids samples for 30-minute sludge volume determinations in one-liter cylinders; measured temperature, pH and alkalinity of selected samples; measured the depth of the sludge blankets in the three clarifiers; measured and adjusted chemical feed rates as needed; and obtained differential pressure readings on the parallel filters and backwashed them when required.

Sludge wasting on the modified aeration system was accomplished automatically by diverting the recycle flow to a drum with a level control probe; a timer was used to control the frequency of diversion to the drum; and the level control probe switched the recycle flow back to the process after 74.9 liters (19.8 gal) had been added to the drum. Sludge wasting on the other two systems was done manually. Whenever the waste rate was 0.19 m^3/day (50 gpd) or less, the wasting was done once per day. For waste rates in excess of 0.19 m^3/day (50 gpd), wasting was done twice per day in roughly equal amounts.

Throughout the year, samples of mixed liquor were removed periodically for settling tests in 2.3 m x 0.15 m (7.5 ft x 6 inches) diameter stirred columns. The stirring mechanism consisted of two 0.64 cm (1/4 inch) diameter rods that extended the length of the column and rotated around the vertical axis at a rate of 10-14 rph.

On numerous occasions, batch kinetic studies were undertaken in the laboratory to establish the process kinetic rates for nitrification and denitrification. The nitrification studies were performed by mixing a sample (1-2 liters) of the nitrification recycle solids with the effluent from the modified aeration clarifier in a ratio similar to that existing in the process at the time. A water bath was employed to insure that the temperature of the kinetic analysis remained the same as that which existed in the process. The mixture was aerated and the decrease in NH_3 was monitored by Technicon analyses. In all cases, the NH_3 removal followed zero order kinetics and the rate of removal was determined per unit of mixed-liquor volatile suspended-solids. The change in mixed-liquor solids concentration during the course of the kinetic study was insignificant.

The denitrification kinetic studies were performed by mixing 1-2 liters of denitrification recycle solids with a sample of the nitrification effluent in a ratio similar to that which existed in the process. Methanol was also added. A flexible, plastic screw top container was used to hold the mixture and the container was "squeezed" to exclude all air prior to putting on the plastic cap. A large magnet and magnetic stirrer was used to keep the contents thoroughly mixed and a sample was continuously withdrawn for $(NO_2 + NO_3)$-N analysis by a Technicon autoanalyzer. A water bath was employed to insure that the temperature remained the same as that which prevailed in the actual denitrification process at the time. The decrease in $(NO_2 + NO_3)$-N followed zero order kinetics in all cases and the rate was expressed per unit of volatile suspended solids.

SECTION VI

RESULTS AND DISCUSSIONS

The average monthly characteristics of the District of Columbia primary effluent are summarized in Table 1. The wastewater is largely of domestic origin with very little industrial discharge. The presence of a combined sewer system plays a significant part in the monthly variation indicated. In spite of the overloaded primary clarifiers (Table 2), the primary wastewater is relatively weak with an average BOD of 103 mg/l and a COD of 236 mg/l. The TKN averaged 23.7 mg/l and 15.6 mg/l of this was present as NH_3-N. The influent (NO_2 + NO_3)-N content was negligible. Influent PO_4 averaged 20.8 mg/l.

As indicated in Figure 4, the modified aeration reactor solids were varied throughout the year to produce the desired effluent quality. The large variation in necessary reactor solids results from winter wastewater temperatures of about 15°C versus summer wastewater temperatures of 26°C. To insure the development of a sufficient quantity of heterotrophic organisms for good floc formation and settleability in the subsequent nitrification process, the residual effluent BOD was maintained within the range indicated. (The relatively low effluent BOD residual entering nitrification during the last four months of the study, however, did not adversely affect the settling performance of the nitrification system.)

The volatile solids concentration ranged between 61-66% of the MLSS. This low volatile solids content reflects the inert solids buildup resulting from ferric chloride addition. As indicated in Table 3, the ferric chloride dosage was uniform throughout most of the project period. The average dosage was 36 mg/l, which produced a ferric to influent phosphorus mole ratio of 1:1. The combination of chemical precipitation and biological uptake resulted in an overall average phosphorus removal of 72.3%.

Although a considerable portion of the influent carbonaceous material and phosphate was removed in the modified aeration process, the average reduction in total nitrogen was only 7.4 mg/l (Figure 5). Of this, organic nitrogen removal accounted for the major decrease in TKN. Since the process was operated at a sludge retention time (SRT) that varied from 0.65 days to 1.3 days during the year's operation, there was no opportunity for a nitrifying population to develop. Consequently, the effluent (NO_3 + NO_2)-N concentration was negligible throughout the year.

The results presented in Table 4 summarize the settling rates obtained from the 0.15 m (6 inch) column studies. The combination of relatively low reactor solids and the addition of ferric chloride produced a sludge with excellent settling characteristics. The monthly variation in effluent suspended solids is summarized in Table 5.

The effluent BOD and phosphate residuals from the nitrification system and the variations in mixed liquor volatile solids throughout the year's operation are presented in Figure 6. The large decrease in reactor solids

Table 1. AVERAGE MONTHLY CHARACTERISTICS OF DISTRICT OF COLUMBIA PRIMARY EFFLUENT

	TOC	COD	BOD	TKN	NH_3-N	PO_4	SS	VSS
OCTOBER	73	251	115	26.2	17.8	23.5	95	70
NOVEMBER	61	239	106	24.5	16.9	21.9	112	81
DECEMBER	61	238	100	26.8	16.4	20.7	115	78
JANUARY	69	246	97	25.7	16.7	22.2	106	77
FEBRUARY	69	234	99	23.5	15.5	21.8	108	82
MARCH	79	263	110	24.8	14.1	21.7	128	97
APRIL	68	230	99	21.7	13.3	19.1	120	85
MAY	79	234	115	23.3	14.9	21.2	109	80
JUNE	77	238	111	23.0	14.7	21.8	111	83
JULY	66	221	96	21.6	15.5	18.2	101	75
AUGUST	63	207	88	20.7	15.0	16.9	102	79
SEPTEMBER	--	225	99	22.6	16.4	21.1	110	85

All concentrations in mg/l.

Table 2. PRIMARY CLARIFIER LOADINGS AND AVERAGE PROCESS FLOW

	Average Loading On D.C. Primary Clarifier m/day	Average Process Flow m^3/day
OCTOBER	83	175
NOVEMBER	--	240*
DECEMBER	90	210
JANUARY	87	205
FEBRUARY	88	200
MARCH	88	200
APRIL	91	200
MAY	88	205
JUNE	--	200
JULY	87	215
AUGUST	88	210
SEPTEMBER	88	215

* Includes 4 days of 380 m^3/day operation to simulate rain peaks.

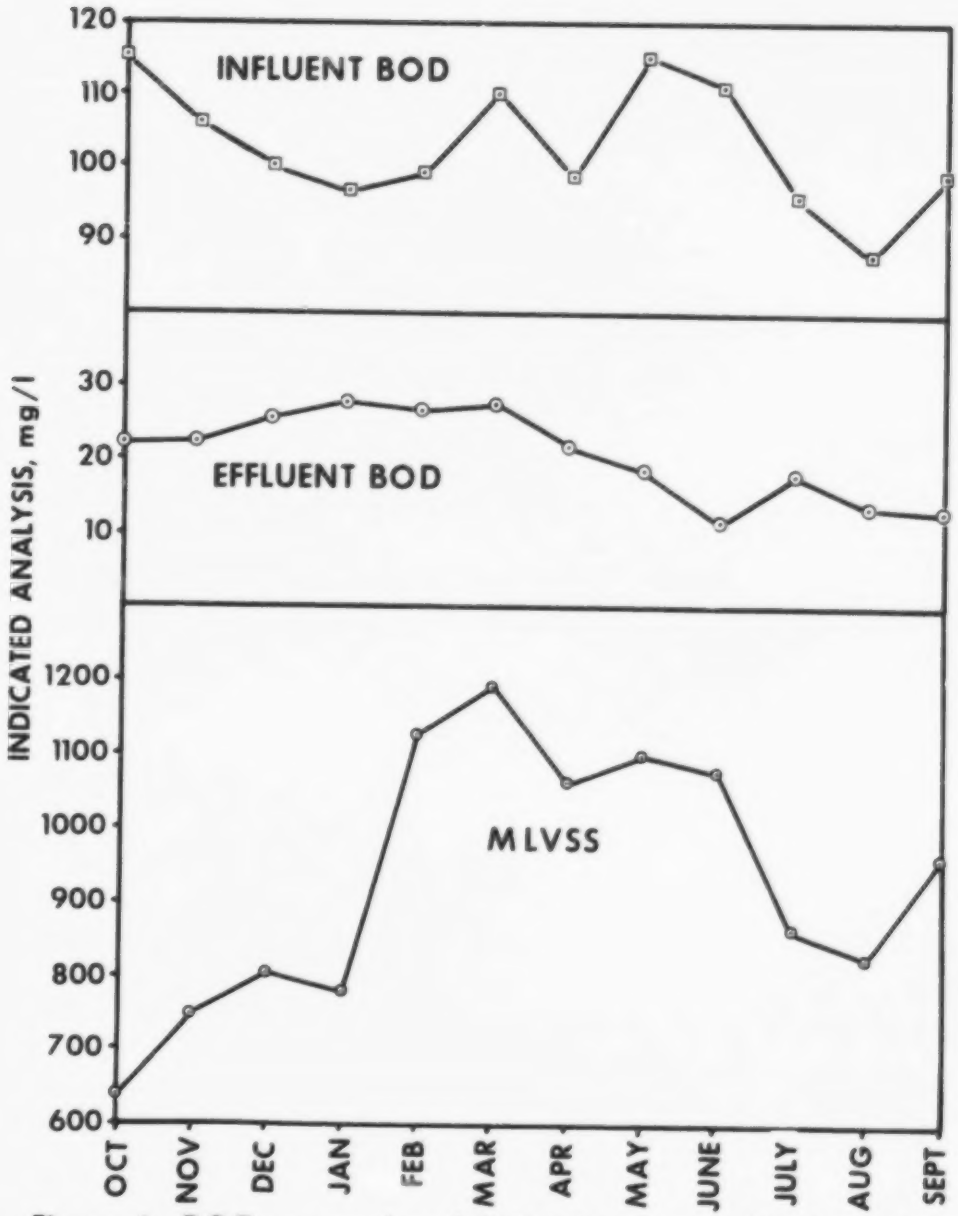

Figure 4. BOD removal and MLVSS in the modified aeration system

Table 3. FERRIC CHLORIDE DOSAGES AND PHOSPHORUS REMOVAL FOR MODIFIED AERATION

	$FeCl_3$ Dose mg/l	PO_4, Inf. mg/l	PO_4, Eff. mg/l	PO_4 % Removal	Fe:P Mole Ratio
OCTOBER	47	23.5	5.6	76.2	1.17:1
NOVEMBER	37	21.9	5.0	77.2	0.99:1
DECEMBER	35	20.7	6.2	70.0	0.99:1
JANUARY	37	22.2	6.3	71.6	0.98:1
FEBRUARY	36	21.8	7.1	67.4	0.97:1
MARCH	35	21.7	7.4	65.9	0.94:1
APRIL	34	19.1	6.5	66.0	1.04:1
MAY	37	21.2	6.2	70.8	1.02:1
JUNE	35	21.8	4.3	80.3	0.94:1
JULY	32	18.2	5.0	72.5	1.03:1
AUGUST	35	16.9	4.9	71.0	1.21:1
SEPTEMBER	35	21.1	4.8	77.3	0.97:1

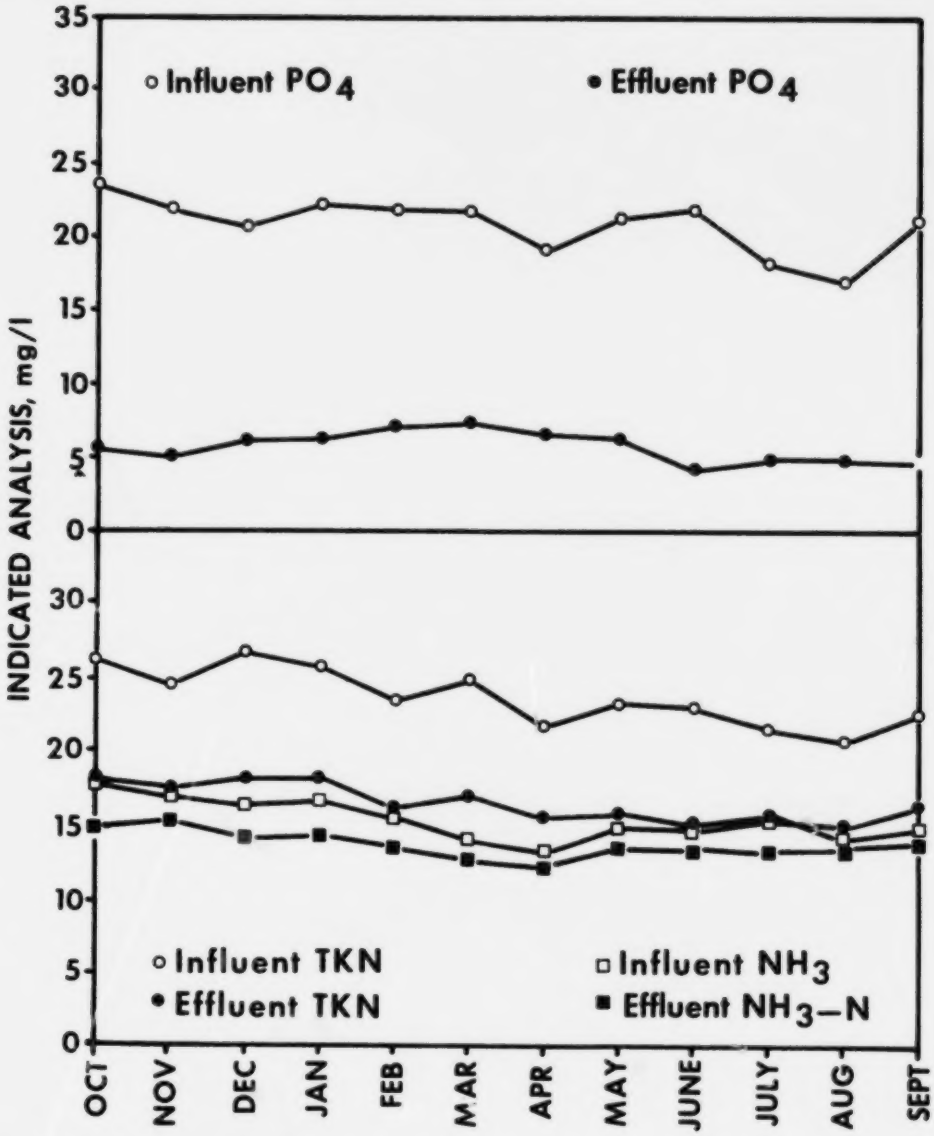

Figure 5. Phosphorus and nitrogen removals in the modified aeration system

Table 4. SLUDGE VOLUME INDEX AND SETTLING CHARACTERISTICS OF THE MODIFIED AERATION ACTIVATED SLUDGE

	Process SVI ml/gm	Settling Test Results m/hr	°C	MLSS mg/l
OCTOBER	89	8.4	25	1300
		6.6	22.2	1250
		7.0	22.2	1200
NOVEMBER	80	6.8	21.7	1500
DECEMBER	67	10.7	17.8	1850
JANUARY	69	8.0	16.7	1200
		7.3	16.7	1350
		12.6	16.4	1050
FEBRUARY	73	7.4	13.5	1850
		7.4	14.0	2100
		13.7	15	1100
MARCH	71	12.0	15	1800
		10.7	14.5	2000
APRIL	68	16.6	15.5	1650
		10.2	16	1600
MAY	80	9.8	18	1350
		7.3	18	1650
		13.3	21	1800
JUNE	103	6.4	23.5	1800
		9.3	19.5	1700
JULY	96	4.2	25.5	1850
		8.7	24.5	1150
		11.4	24.7	1300
AUGUST	94	4.3	25.5	1300
		5.9	27	1450
		11.9	23.5	1500
SEPTEMBER	106	5.5	22.5	1450
		6.1	24	1550

Table 5. AVERAGE MONTHLY CHARACTERISTICS OF MODIFIED AERATION CLARIFIED EFFLUENT

	TOC	COD	BOD	TKN	NH_3-N	PO_4	SS	VSS
OCTOBER	28	61.5	22.3	17.7	14.8	5.58	21	15
NOVEMBER	26	75.7	22.5	17.4	15.3	5.04	32	22
DECEMBER	29	84.7	25.8	18.2	14.1	6.19	33	23
JANUARY	26	74.5	28.0	18.3	14.4	6.25	33	20
FEBRUARY	28	70.6	26.8	16.2	13.5	7.10	31	23
MARCH	28	78.3	27.6	17.1	12.7	7.44	38	27
APRIL	24	65.3	21.9	15.5	12.3	6.50	31	20
MAY	23	55.9	18.8	15.8	13.6	6.23	22	16
JUNE	19	42.3	11.7	14.9	13.6	4.30	13	10
JULY	19	51.3	18.1	15.4	13.3	5.00	20	14
AUGUST	19	46.7	13.9	13.9	13.6	4.88	17	13
SEPTEMBER	--	43.9	13.2	14.9	13.8	4.76	18	13

All concentrations in mg/l.

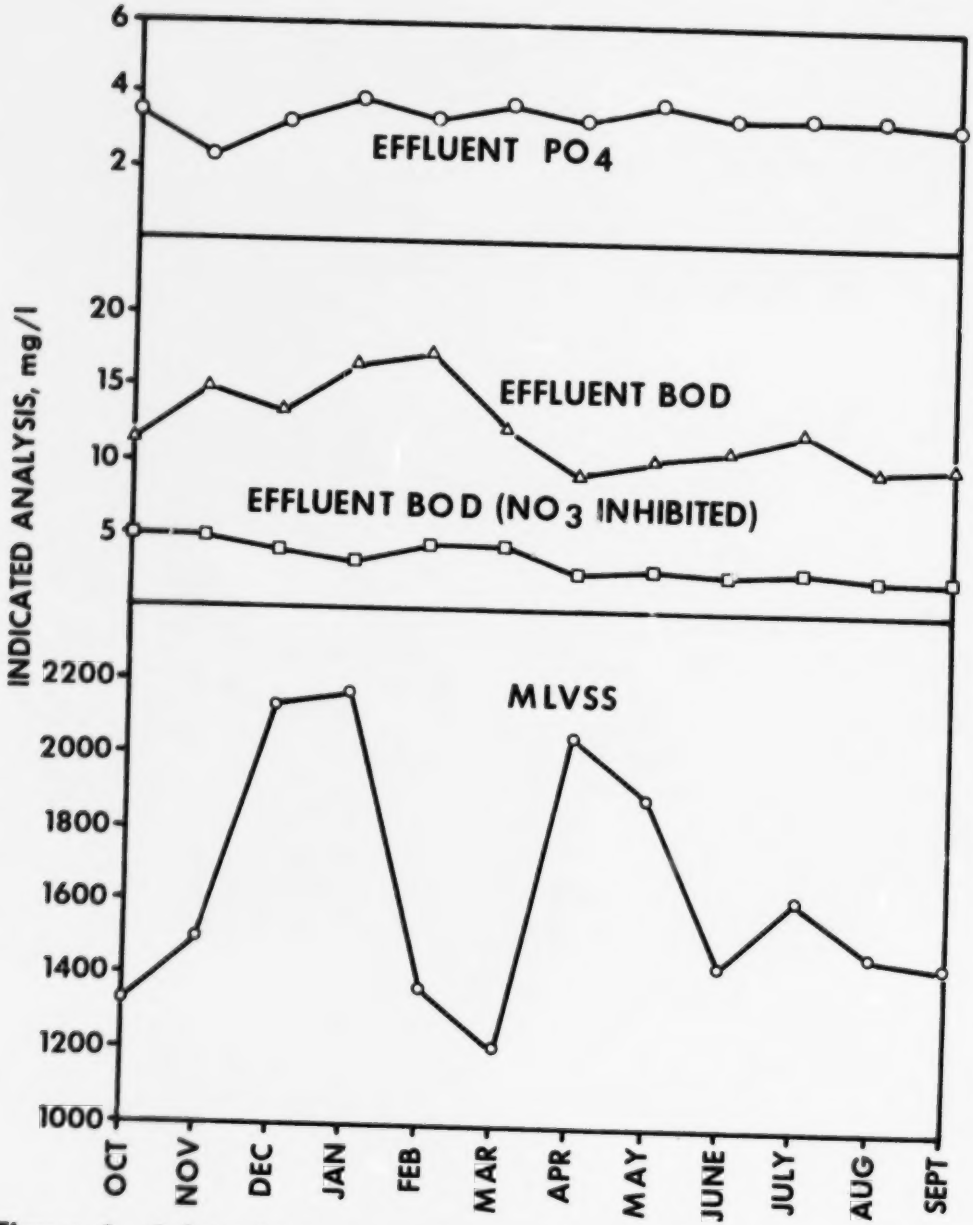

Figure 6. Selected process parameters for the nitrification system

indicated for February and March was the result of a pump failure in February and the concomitant loss of a substantial portion of the solids stored in the clarifier. This loss resulted in the lower-than-desired solids levels for winter operation. The mixed-liquor volatile suspended-solids varied from a low of 48% to a high of 64% of the mixed liquor suspended solids.

As previously indicated, dry lime (CaO) was added to the first pass of the nitrification reactor in sufficient quantity to provide an effluent pH of 7.0-7.2. Since the D.C. wastewater is of low alkalinity (∿ 100 mg/l as $CaCO_3$ after modified aeration), the natural buffer capacity is not sufficient to prevent pH depression resulting from the nitric acid produced during nitrification. The average lime dose for the year was 60 mg/l. Inert material present in the lime was responsible for the relatively low percentage of mixed-liquor volatile suspended-solids observed. No attempt was made to evaluate the nitrification process under natural pH conditions. However, it is quite likely that one could reduce the lime dosage and operate at somewhat lower pH values without a significant decrease in nitrification kinetics.

The inhibited BOD values indicated in Figure 6 represent the average of a maximum of eight samples for any given month. Whereas the inhibited BOD analysis was performed approximately twice per week, the normal effluent BOD values represent the average of daily analyses taken throughout the month. This difference in the data base was responsible for much of the variation in the relative differences between the inhibited and normal BOD values. The nitrified effluent was essentially free of carbonaceous BOD. The effluent phosphate concentration was very steady throughout the year and averaged 3.40 mg/l. Other effluent parameters are summarized in Table 6.

The large solids loss in February was responsible for the relatively high TKN and NH_3-N levels in the nitrification effluent during part of February and March. Except for this temporary effluent deterioration resulting from mechanical failure, the nitrification process functioned very well throughout the year (Figure 7). Excluding the February and March data, the average effluent TKN and NH_3-N values were 1.21 mg/l and 0.63 mg/l, respectively. For the entire year's operation, the effluent TKN averaged 1.72 mg/l; the NH_3-N, 1.15 mg/l.

A summary of the nitrification kinetic rates determined from the laboratory batch studies is presented in Figure 8. The results include all kinetic constants obtained from the system and cover nearly two years of operation. The kinetic rate was significantly influenced by process temperature. In fact, treating the kinetic rate as a function of just the temperature produces a linear correlation coefficient of 0.837. Other factors, such as variation in the BOD to TKN ratio and operation at different SRT's also influenced the kinetic rate and account for some of the variation shown by examining the rate as a simple function of temperature. Nonetheless, the temperature dependency is quite obvious.

Table 6. AVERAGE MONTHLY CHARACTERISTICS OF NITRIFICATION CLARIFIED EFFLUENT

	TOC	COD	BOD	TKN	NH_3-N	NO_3-N	PO_4	SS	VSS
OCTOBER	7.1	20.0	11.3	0.69	0.38	14.4	3.50	5	4
NOVEMBER	9.1	29.6	14.8	2.80	1.42	11.8	2.28	9	5
DECEMBER	10.5	26.4	13.3	1.82	1.01	10.4	3.24	11	6
JANUARY	8.6	23.4	16.6	1.56	0.65	13.1	3.90	12	6
FEBRUARY	11.9	23.8	17.4	4.74	4.51	9.0	3.38	9	5
MARCH	9.0	24.4	12.3	3.75	2.98	10.6	3.79	8	5
APRIL	6.5	19.1	9.2	1.05	0.66	12.4	3.40	7	4
MAY	8.2	16.9	10.2	0.68	0.24	12.7	3.83	7	4
JUNE	7.5	17.6	10.9	0.76	0.16	13.4	3.42	8	5
JULY	6.9	17.2	12.3	0.91	0.77	12.5	3.43	7	4
AUGUST	6.9	16.4	9.7	0.70	0.32	12.1	3.41	7	5
SEPTEMBER	---	17.3	10.1	1.14	0.64	12.2	3.24	8	5

All concentrations in mg/l.

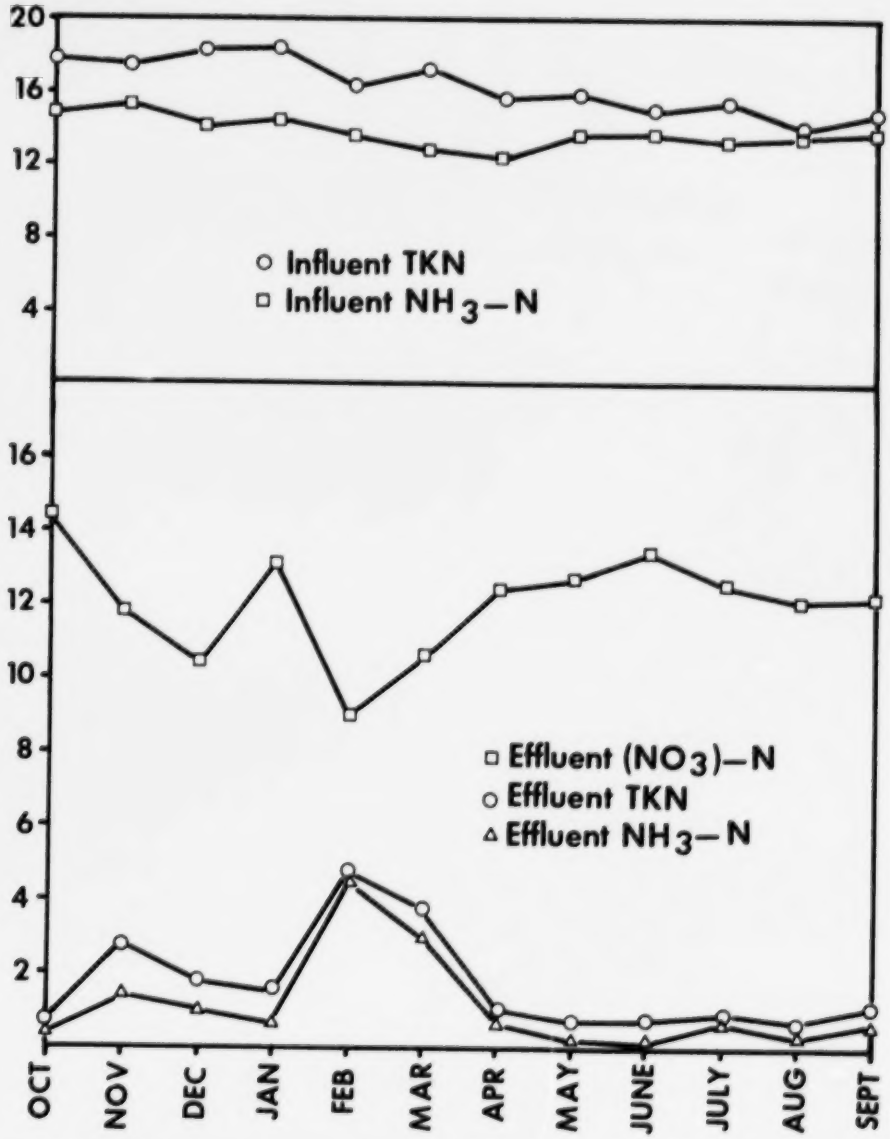

Figure 7. Changes in nitrogen concentrations in the nitrification process

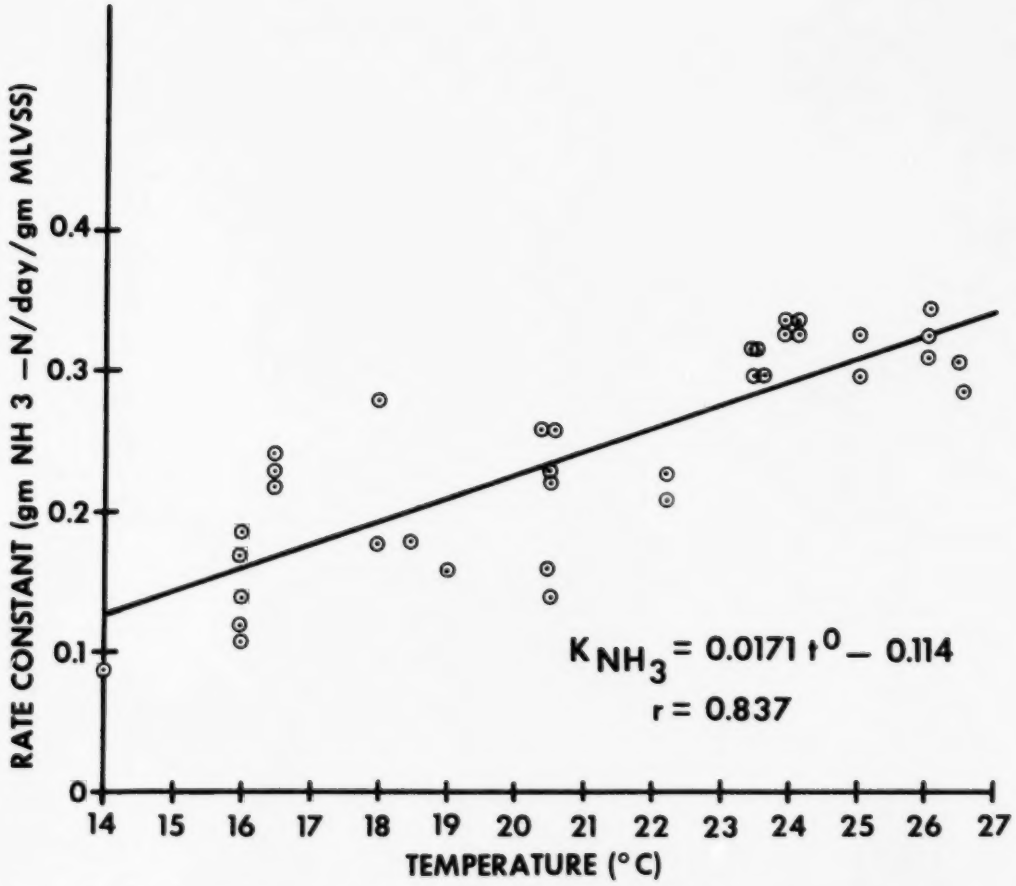

Figure 8. Summary of nitrification kinetic data from January 1972 to September 1973

The results of the 0.15 m (6 inch) column settling studies are summarized in Table 7. During winter operation, the process SVI was higher and the settling velocities lower than during summertime operation. This is just the reverse of the modified aeration process, where the increased filamentous growth during the summer produced somewhat higher SVI's and lower settling velocities than in the winter months.

The nitrogen transformations occurring in the denitrification activated sludge are indicated in Figure 9. There was a very small decline in the NH_3-N concentration. A slight increase in effluent TKN resulting from a greater solids concentration in the effluent than in the influent (Table 8) also occurred. For all practical purposes, however, there was no significant change in the TKN or NH_3 levels in the effluent when compared with the denitrification influent. Denitrification reduced the influent NO_3-N (NO_2 analyses were performed three times per week but no more than trace quantities were ever detected) from an average of 12.1 mg/l to 0.72 mg/l and effected an overall average removal of 94%. To obtain these nitrogen removals, the denitrification process was operated at MLVSS levels that varied between 1350 and 2400 mg/l (Figure 10). The volatile suspended solids comprised between 53 to 60% of the mixed liquor solids. These concentrations resulted from process SRT's that varied from 10 to 19 days.

In order to obtain denitrification, it was necessary to add a degradable carbon source to support heterotrophic growth. Once the dissolved oxygen present in the influent wastewater was removed, the oxygen bound in the NO_3 molecule served as the terminal hydrogen acceptor and the nitrate nitrogen was converted to nitrogen gas.

The average monthly methanol dosages, NO_3 removals, and methanol dose per unit of NO_3-N removed are summarized in Table 9. No sustained attempt was made to reduce the methanol dosage to the minimum amount needed. Rather, the difficulty of accurately controlling the feed rate on a small scale and other problems resulted in a tendency to feed more methanol than actually needed. For this reason the methanol dosages for some months were higher than actually required. In spite of this, there were several occasions when excess nitrate was present in the effluent because of short periods of insufficient methanol. A dose of four units of methanol (by weight) per unit of NO_3-N removed seemed to be the upper limit of the amount actually required.

The effluent PO_4 concentration and effluent BOD's are also presented in Figure 10. As was the case for the nitrification process, the inhibited BOD values are based on about 25% of the number of samples comprising the uninhibited BOD average. This difference in the data base accounts for some of the deviation shown. Since the denitrification process included a terminal aerated chamber, the difference between influent and effluent BOD is not an indication of possible methanol overdosing.

The influent and effluent phosphate concentration and the average monthly alum dosages are summarized in Table 10. The Al:P mole ratio varied between 3:1 and 5:1 with no direct correlation between alum dosage and

Table 7. SLUDGE VOLUME INDEX AND SETTLING CHARACTERISTICS OF THE NITRIFICATION ACTIVATED SLUDGE

	Process SVI ml/gm	Settling Test Results m/hr	^{o}C	MLSS mg/l
OCTOBER	104	5.6	21.7	2600
		5.0	22.2	2100
		4.7	21.7	2300
NOVEMBER	124	4.3	21.4	2600
DECEMBER	150	2.1	17.8	3200
		1.7	17.8	2400
		1.7	17.5	3200
JANUARY	182	2.7	16.1	3800
		2.4	17.2	3400
		2.6	16.7	4000
FEBRUARY	165	2.5	14.0	3000
		5.3	14.0	1600
		3.3	14.5	2000
MARCH	151	3.8	17.5	1900
		4.8	15.5	1800
		5.0	15.3	1800
APRIL	189	2.1	15.5	3200
		1.8	15.5	3500
		2.0	17.5	3900
MAY	138	2.2	17.0	3800
		2.8	19.0	3000
		8.6	19.5	2900
JUNE	81	4.8	22.0	2900
		4.7	23.5	3600
		4.2	23.5	2800
JULY	84	5.7	26.5	2600
		4.8	25.0	3900
		5.2	23.5	2800
AUGUST	76	4.8	26.0	3400
		5.7	26.0	3400
		5.7	24.0	2500
SEPTEMBER	76	4.7	22.0	2900

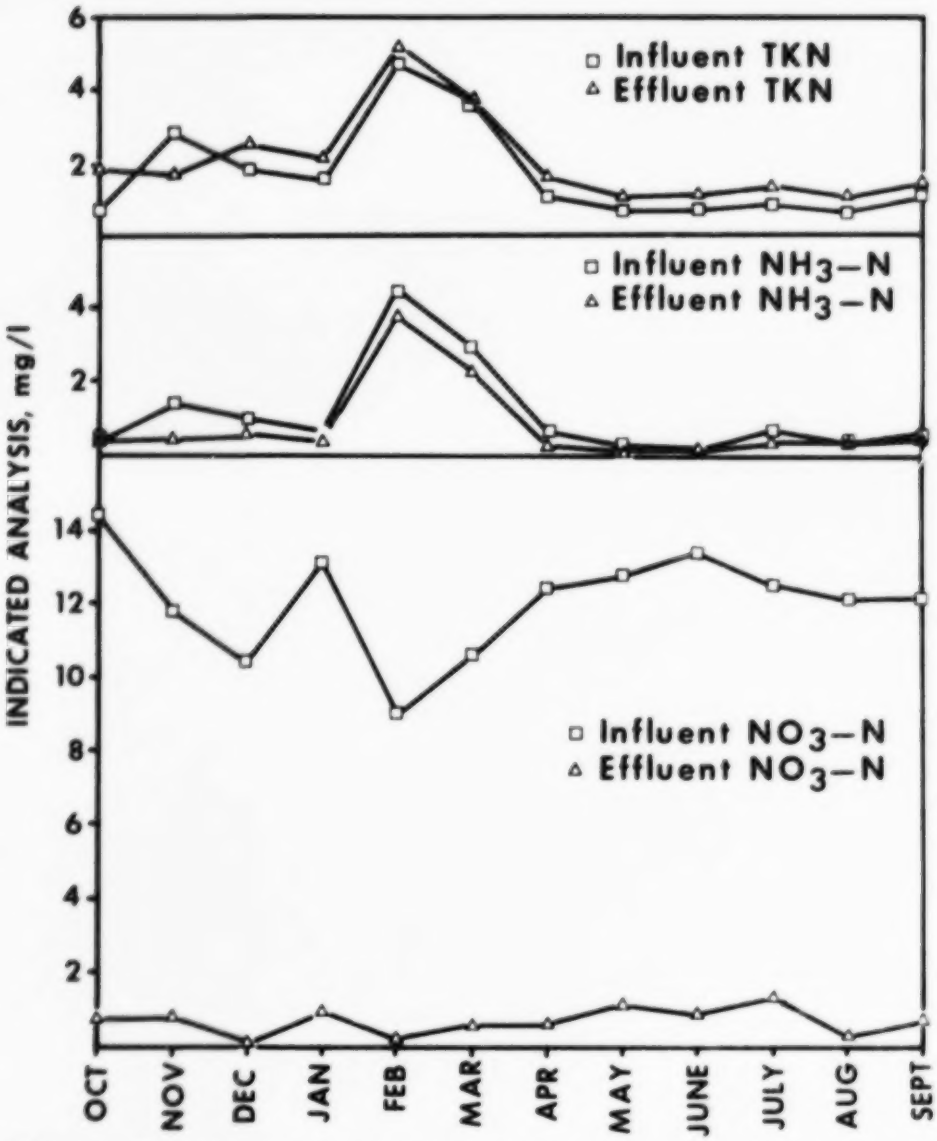

Figure 9. Changes in nitrogen concentrations in the denitrification process

Table 8. AVERAGE MONTHLY CHARACTERISTICS OF DENITRIFICATION CLARIFIED EFFLUENT

	TOC	COD	BOD	TKN	NH_3-N	NO_3-N	PO_4	SS	VSS
OCTOBER	9.9	28.4	9.5	1.79	0.41	0.77	2.43	17	9
NOVEMBER	10.3	30.3	8.4	1.66	0.53	0.80	1.10	18	10
DECEMBER	12.9	37.2	11.0	2.50	0.62	0.11	1.85	21	13
JANUARY	10.4	27.7	12.5	2.13	0.38	0.98	2.10	19	9
FEBRUARY	15.9	33.3	13.9	5.19	3.80	0.25	2.54	25	15
MARCH	11.0	27.9	10.1	3.69	2.33	0.61	2.48	19	11
APRIL	8.9	24.2	7.4	1.62	0.26	0.61	2.26	21	10
MAY	8.8	19.0	7.4	1.03	0.08	1.17	2.27	16	9
JUNE	8.8	19.1	8.5	1.11	0.17	0.88	1.98	14	7
JULY	8.0	20.4	10.2	1.38	0.39	1.38	2.22	19	9
AUGUST	7.8	19.3	6.8	1.10	0.35	0.30	1.82	16	10
SEPTEMBER	---	21.5	7.6	1.53	0.48	0.77	2.25	18	11

All concentrations in mg/l.

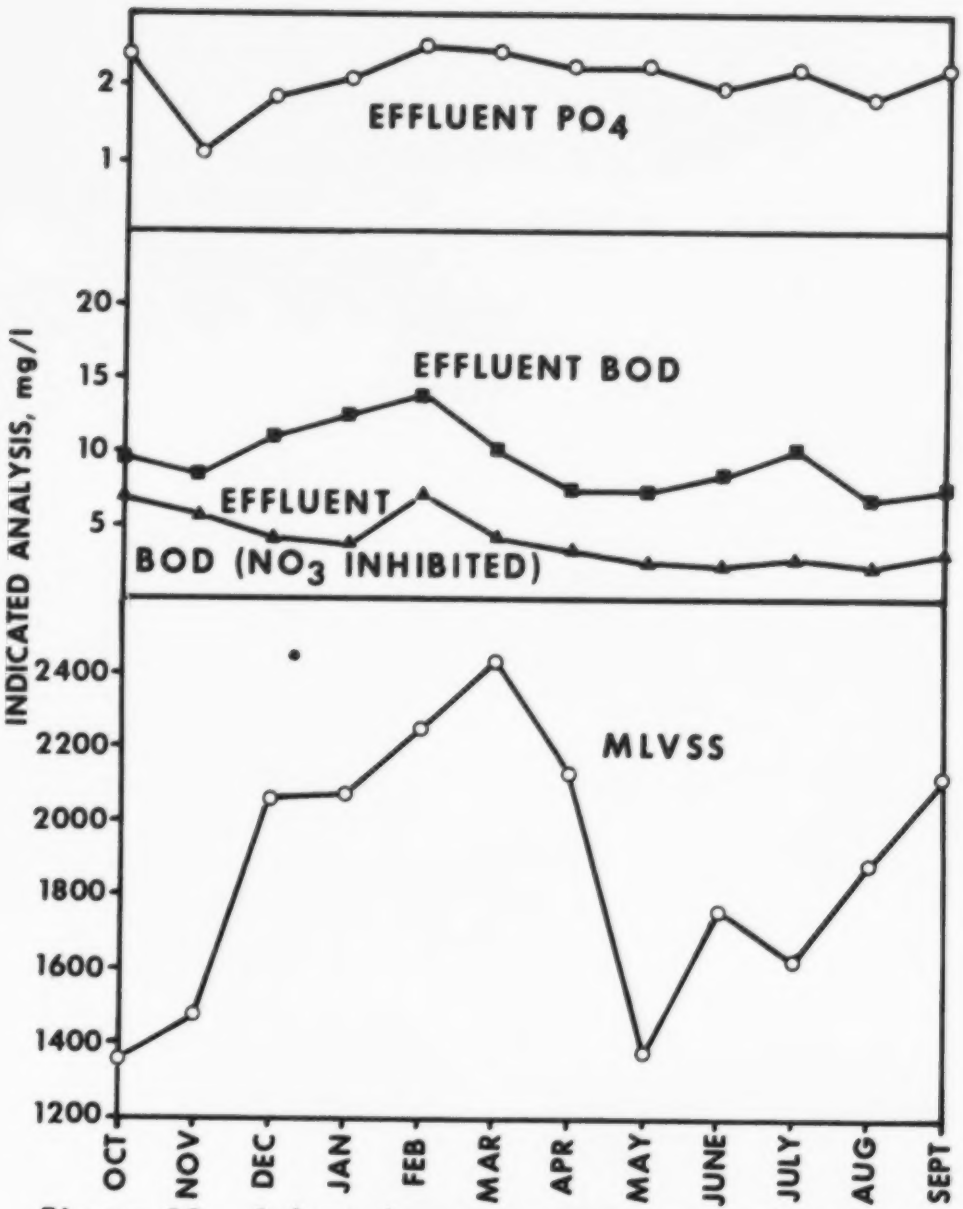

Figure 10. Selected process parameters for the denitrification system

Table 9. METHANOL DOSAGES AND NITRATE REMOVAL FOR DENITRIFICATION

	Methanol Dose mg/l	NO_3-N, Inf. mg/l	NO_3-N, Eff. mg/l	NO_3-N Removed mg/l	Methanol Dose ÷ NO_3-N Removed
OCTOBER	67	14.4	0.8	13.6	4.9
NOVEMBER	55	11.8	0.8	11.0	5.0
DECEMBER	49	10.4	0.1	10.3	4.8
JANUARY	46	13.1	1.0	12.1	3.8
FEBRUARY	48	9.0	0.3	8.7	5.5
MARCH	49	10.6	0.6	10.0	4.9
APRIL	46	12.4	0.6	11.8	3.9
MAY	47	12.7	1.2	11.5	4.1
JUNE	46	13.4	0.9	12.5	3.7
JULY	46	12.5	1.4	11.1	4.1
AUGUST	56	12.1	0.3	11.8	4.7
SEPTEMBER	54	12.2	0.8	11.4	4.7

Table 10. ALUM DOSAGES AND PHOSPHORUS REMOVAL FOR DENITRIFICATION

	Alum Dose mg/l	PO_4, Inf. mg/l	PO_4, Eff. mg/l	PO_4 % Removal	Al:P Mole Ratio
OCTOBER	41	3.50	2.43	30.6	3.7:1
NOVEMBER	35	2.28	1.10	51.8	4.9:1
DECEMBER	33	3.24	1.85	42.9	3.3:1
JANUARY	35	3.90	2.10	46.2	2.9:1
FEBRUARY	37	3.38	2.54	24.9	3.5:1
MARCH	35	3.79	2.48	38.8	3.0:1
APRIL	37	3.40	2.26	33.5	3.5:1
MAY	38	3.83	2.27	40.7	3.2:1
JUNE	42	3.42	1.98	42.1	3.9:1
JULY	39	3.43	2.22	35.3	3.6:1
AUGUST	44	3.41	1.82	46.6	4.1:1
SEPTEMBER	47	3.24	2.25	30.6	4.6:1

effluent PO_4 concentrations. This lack of correlation largely resulted from the variations in clarification efficiency during the year. The real impact of the alum dosage was in insuring good phosphate removal on the filters receiving the effluent from the denitrification clarifier.

The settling characteristics of the denitrification system were entirely satisfactory throughout the year (Table 11). The lowest rates obtained were nearly 3 m/hr.

The denitrification kinetic rate constants determined in laboratory batch studies are presented in Figure 11. In contrast to the strong correlation between kinetic rate and temperature in the nitrification kinetic studies, the denitrification kinetic constants exhibit a relatively weaker correlation when considered as just a function of the single variable temperature. The data points shown between 14 and 18.5°C and grouped below the regression line (a total of 11 values) are kinetic rates obtained in earlier operations during the winter of 1972 when there was considerable methanol overdosing (2 to 3 times the required dose) and high SRT operation. Both of these factors contributed to these low kinetic rates.

The changes in BOD, total nitrogen, and PO_4 as a result of filtration are presented in Figure 12. These values represent the average effluent quality from the dual- and multi-media filters. The filters were not operated during February. Although the denitrification effluent meets the proposed discharge standards for total nitrogen, it does not meet the proposed standards for BOD or PO_4. The addition of the filtration step, however, produced an overall average BOD of 2.0 mg/l, total nitrogen of 1.6 mg/l, and total phosphate of 0.52 mg/l. The phosphate concentration could be decreased further by feeding more alum ahead of filtration. Generally the multi-media filters produced a slightly improved effluent quality, with typical improvements usually not exceeding 5%. Filter runs of 24 hours were normally obtained with either media. The filtration results have been presented in detail elsewhere.[5]

Table 11. SLUDGE VOLUME INDEX AND SETTLING CHARACTERISTICS OF THE DENITRIFICATION ACTIVATED SLUDGE

	Process SVI ml/gm	Settling Test Results m/hr	^{o}C	MLSS mg/l
OCTOBER	85	4.5	22.2	2400
		3.7	23.3	2800
NOVEMBER	82	3.3	21.4	1600
DECEMBER	71	4.3	17.8	3300
JANUARY	76	3.9	16.7	3800
		3.3	17.2	3600
		3.6	17.0	3900
FEBRUARY	72	2.7	13.5	4100
		3.0	14.5	3900
		3.3	15	3300
MARCH	79	2.9	15.5	4400
		3.0	16	4300
		3.4	14.5	4000
APRIL	79	2.9	15.5	4100
		3.0	16	4100
		4.5	16	2800
MAY	81	4.4	18	2500
		4.0	20	2500
		5.2	17	2300
JUNE	61	5.3	20.5	2800
		4.7	24.5	3000
		6.3	23.5	3500
JULY	54	6.5	26.5	3000
		7.1	26	2600
		7.1	25.5	2800
AUGUST	55	3.7	25.5	3800
		5.4	27.7	3100
SEPTEMBER	56	4.8	24	3600
		5.7	24	4100

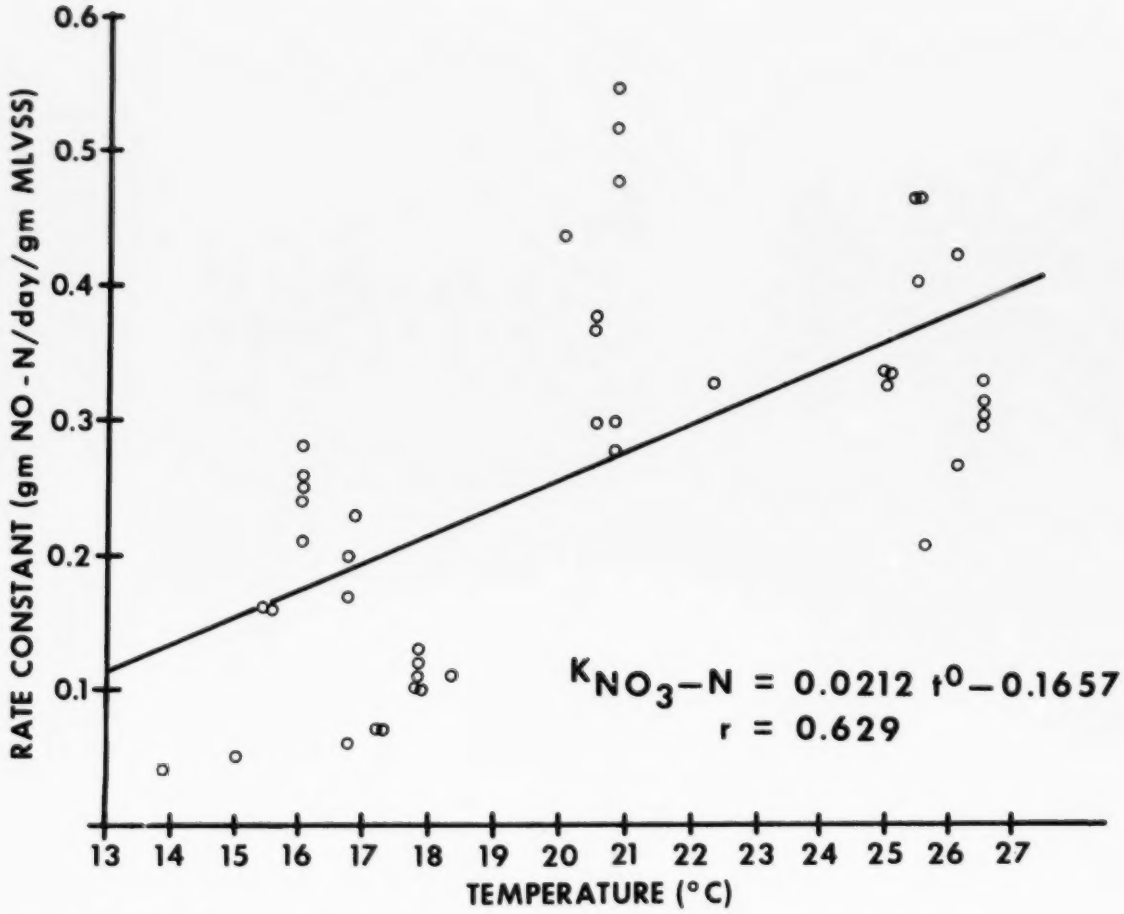

Figure 11. Summary of denitrification kinetic data from January 1972 to September 1973

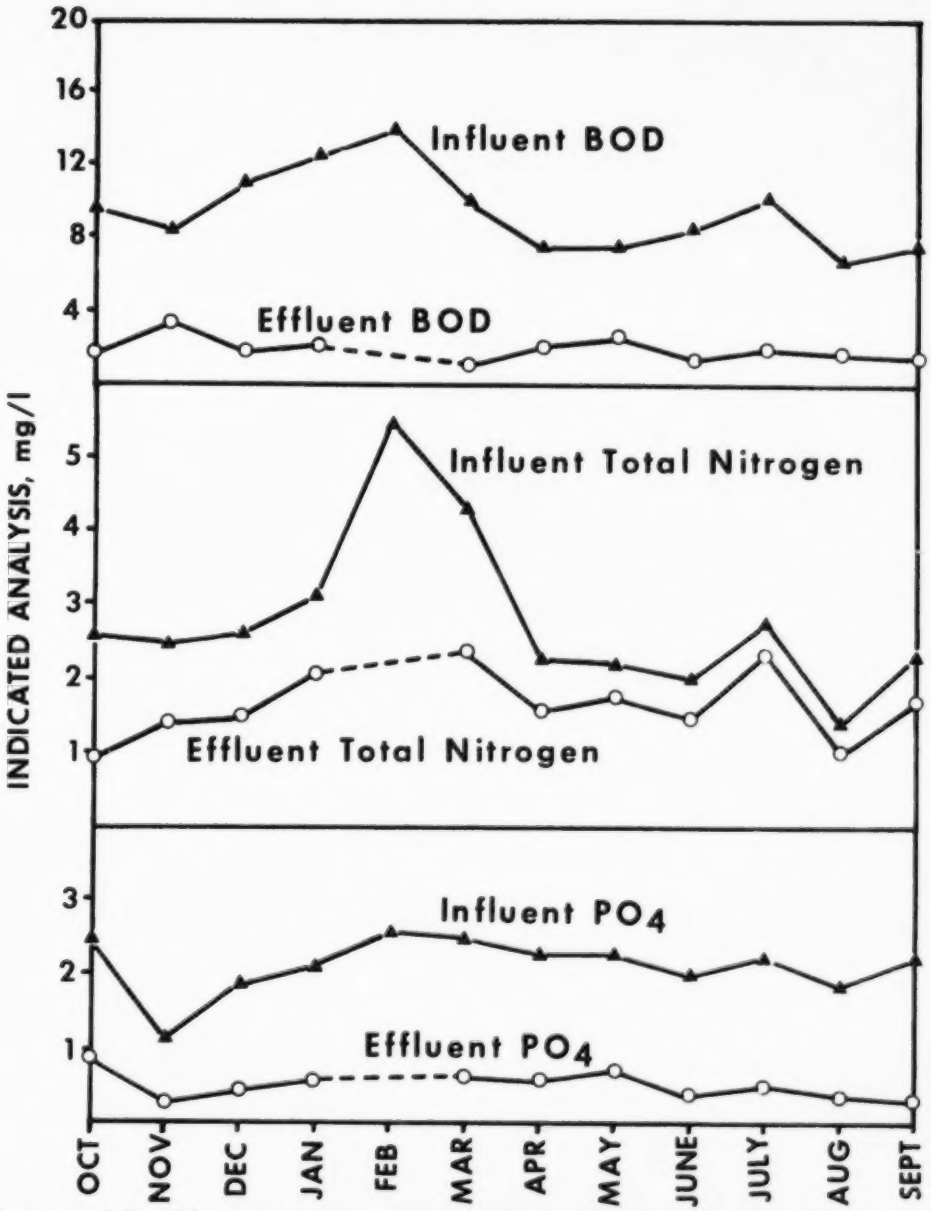

Figure 12. Changes in BOD, nitrogen and phosphorus resulting from filtration.

SECTION VII

REFERENCES

1. Barth, E. F., Brenner, R. C., and Lewis, R. F., "Chemical-Biological Control of Nitrogen and Phosphorus in Wastewater Effluent," Jour. Water Poll. Control Fed., 44, 2040 (1968).

2. "Standard Methods for the Examination of Water and Wastewater." 13th ed., American Public Health Association, New York (1971).

3. "Methods for Chemical Analysis of Water and Waste." Report No. 16020-07/71, U.S. EPA, Cincinnati, Ohio (1971).

4. Gales, M., Julian, E. C., and Kroner, R. C., "Method for Quantitative Determination of Total Phosphorus in Water," Jour. of Am. Water Wks. Assoc., 58, 1363 (1966).

5. O'Farrell, T. P., and Bishop, S. L., "Filtration of Effluent from Staged Nitrification-Denitrification Treatment," presented at the 76th National AIChE Meeting, March 10-13, 1974, in Tulsa, Oklahoma.

SECTION VIII

PUBLICATIONS

Heidman, J. A., Bishop, D. F., and Stamberg, J. B., "Carbon, Nitrogen, and Phosphorus Removal in Staged Nitrification Activated Sludge Treatment," AIChE Symposium Series 145, Water 1974, 71 , 264 (1975).